The change of electric field and of some other insulating properties during isochronal annealing in thermally poled Ge-doped silica films

Liu, Q.M.; Poumellec, B.; Braga, D.; Blaise, G.; Ren, Yitao; Kristensen, Martin

Published in:
Applied Physics Letters

Link to article, DOI:
10.1063/1.2053361

Publication date:
2005

Document Version
Publisher's PDF, also known as Version of record

The change of electric field and of some other insulating properties during isochronal annealing in thermally poled Ge-doped silica films

Qiming Liu[a] and Bertrand Poumellec
Laboratoire de Physico-Chimie de l'Etat Solide, UMR8648 CNRS-UPS, Université de Paris Sud, F-91405 Orsay Cedex, France

Delfin Braga and Guy Blaise
Physique des Solides, UMR8502 CNRS-UPS, Université de Paris Sud, F-91405 Orsay Cedex, France

Yitao Ren[b] and Martin Kristensen[c]
Research Center COM, Technical University of Denmark, Building 345v, DK-2800Kgs. Lyngby, Denmark

(Received 28 April 2005; accepted 12 August 2005; published online 12 September 2005)

The secondary electron emission contrast between poled and unpoled regions in thermally poled Ge-doped silica films were measured according to different annealing temperatures and electron doses with electron acceleration energy of 5 keV. It is used for measuring the change on annealing of poling induced electric field and other insulating properties like electron traps population and conductivity in high field. Concerning the change of the contrast at low dose arising from the poling electric field, we show that this field begins to disappear at around 450 °C and is erased completely at 650 °C. Using a larger dose allows measuring the change in conductivity contrast. We find a stability similar to the electric field with a disappearance around 450~650 °C. On the contrary, for intermediate dose, the contrast remains for larger annealing temperature. It allows measuring properties of the electron traps. Their number appears to be modified in the poling process. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2053361]

In glasses, due to their effective centro-symmetry, there is no second order nonlinearity. However, it has been shown that it is possible to record an electric field in the insulating material to obtain such a property, this is the poling process.[1] The induced polarizability is quadratically dependent on the pump electromagnetic wave and the induced coefficient is an effective optical second order nonlinear coefficient $\chi^{(2)}$. This one is commonly believed to arise from the symmetry-breaking recorded electric field acting on the third-order nonlinear susceptibility as follows: $\chi^{(2)}_{\mathrm{eff}}=3E_{\mathrm{DC}}\chi^{(3)}$.[1] Thermally poled silica glass is a material for applications in nonlinear optics and could be widely used in optoelectronics because of its excellent optical properties. Recently, Poulsen *et al.*[2] show a $\chi^{(2)}_{\mathrm{eff}}$ of the order of 0.25 pm/V. For applications like modulators, routers or switches, the amplitude of the electric field E_{DC} recorded in the material has to be strong and stable at the place of the optical waveguides. The stability of the electric field in the poled glasses is, thus, an important factor determining the nonlinear optical properties produced during the poling process. Its investigation will offer the prospect of its enhancement through a better explanation and a deep understanding of the poling process. The distribution of electric field has been investigated by mostly optical methods.[3–6] The resolution of these methods is generally around a few microns and it is not possible to directly measure the electric field close to the surface near the electrode. On the contrary, it is well-known that electron beam is the most available technique to study surfaces and it has already been used to probe the insulating properties of alumina[7] in the first micron beneath the surface by measuring the variation of the secondary electron emission yield (SEEY) on dose.

Scanning electron microscopy (SEM) observations and SEEY measurements at low dose were performed at the electron energy 5 keV in order to probe a depth of 530 nm. The principle of secondary electron emission yield measurements has been described before.[5] It was observed that the thermally poled Ge-doped silica film charges negatively ($\delta<1$) for the energy of 5 keV.[8] In a previous paper, we have proven that the contrast detected in SEEY measurement of the intrinsic yield at the very beginning of electron irradiation (noted δ_0) can be used for detecting the internal electric field left by the poling in the material.[9] In this Letter, we used this method for characterizing the electric field stability in the film deposited on a silicon substrate. On the other hand, as for $E>3$ keV, we have $\delta<1$, therefore, when going on with irradiation, an electron implantation induced electric field is built that leads to an increase of δ towards 1.[9] This increase is due to electron trapping leading to a space charge in the sample. Then, δ reaches a plateau, that is a steady value ($\delta_{\mathrm{st}}<1$). The value of δ_{st} is related to the electron trap depth. If $\delta_{\mathrm{st}}=1$, the depth is large enough to resist against a strong electric field. A departure of δ_{st} from 1 indicates that some detrapping process is taking place, leading to certain conductivity. This is what we can call "conductivity in high field." Thus, we have a method for detecting any change in insulating properties due to thermal poling process and their thermal resistance.

We used Ge-doped silica films (1.1 μm) on silicon prepared by plasma enhanced chemical vapor deposition (PECVD) for our investigation. The films had the following

[a]Present address: Key Laboratory of Silicate Materials Science and Engineering (Wuhan University of Technology), Ministry of Education, Wuhan, Hubei 430070, P.R. China; electronic mail: qmliu@mail.whut.edu.cn

[b]Present address: Center for optical and electromagnetic research, Department of optical engineering, Zhejiang University, Yuquan, Hangzhou 310027, P.R. China.

[c]Present address: Department of Physics and Astronomy, University of Aarhus, Ny Munkegade Building 520, DK-8000 Århus C, Denmark.

0003-6951/2005/87(12)/121906/3/$22.50

compositions: 76±1 mol % SiO_2, 23±1 mol % GeO_2, 1.5±0.5 mol % of O_2 in excess and some ppm of H_2.

Comb shaped aluminum electrodes (~1.2 μm thick) were made on the glass layer through a photoresist mask. A negative voltage ranging from −30 to −100 V was applied for 15 min at 375 °C across the samples during the thermal poling and then the heating was stopped. The poling voltage was kept till the sample was cooled down to the room temperature. Then the Al electrodes were removed in concentrated H_3PO_4 acid for 20 min at 75 °C in order to measure the SEEY without a screening effect.

During the thermal poling, the process induces a strong internal electric field by separating negative and positive ionic charges. Thus, an electric field exists in the poled region and not in the unpoled one. As the SEE yield is sensitive to the internal field, it is expected to observe a contrast due to the difference of the δ_0 values between the two regions. At 5 keV electron energy, it was observed that δ_0 is smaller in the poled regions than in the unpoled ones: the average value of δ_0 is 0.63±0.01 in the unpoled region and in the interval 0.40~0.54 in the poled region. These lower values of δ_0 are due to the poling field directed outward that prevents secondary electrons to escape.[9] Consequently, δ_0 in the poled region is less than that in the absence of the poling field.

It is shown that the SEEY values in the unpoled regions are always larger than those in the poled regions.[9] The difference of SEEY between unpoled and poled regions is larger with small injected doses ($\sigma < 10^5$ pC/cm^2) than with large doses ($\sigma > 10^5$ pC/cm^2). With small injected doses, the SEEY values increase in both regions but the values in the poled regions increase more quickly than those in the unpoled regions. Later the injected dose is increased until the SEEY assumes its saturated values δ_{st} at large doses. From the above results, we can say that the poled and unpoled regions exhibit different charging properties. The difference of the yields in the poled and unpoled regions becomes smaller as the injected dose increases, because the built-in thermally poled electric field is erased during the electron implantation process. After that, the factor that affects the SEEY is no more the thermally poled electric field but the conductivity of the film in high electric field which is related to the depth of the electron traps and/or their numbers.

Going along with increasing annealing temperature allows us performing measurements of the thermal resistance of the insulating properties of the material before and after poling.

Secondary electron emission (SEE) images in Fig. 1 of the thermally poled Ge-doped silica films were recorded isochronously at different annealing temperatures at an electron energy of E=5 keV with 16 pA electron current. We see that the brightness in unpoled regions is larger than in poled regions. For quantification, the secondary electron emission intensity photographs were digitized by means of an image processor. We plotted the SEEY difference between poled and unpoled regions, see Fig. 2. The contrast in the secondary electron images between the poled and unpoled regions decreases with the increase of annealing temperature and almost disappears at ≅650 °C. The film is broken at 950 °C.

For small injected doses, the physical origin of the contrast was the electric field inscripted inside the glass by thermal poling but for large injected doses, the contrast arises from the electrical resistivity in high field. δ_{st}=0.95 in the unpoled region and 0.84 in the poled one showing that the poling process has deteriorated the insulating properties: the residual conductivity in high field is larger after poling.[9] The SEE images collected in Fig. 3 for large dose according to the annealing temperature, show that this difference decreases to zero at 550 °C.

At 550 °C annealing temperature (Fig. 4) the contrast between poled and unpoled regions has almost disappeared at low and large doses (78 and 2064 pC) whereas a strong contrast still subsist at intermediate dose (254 pC). It allows

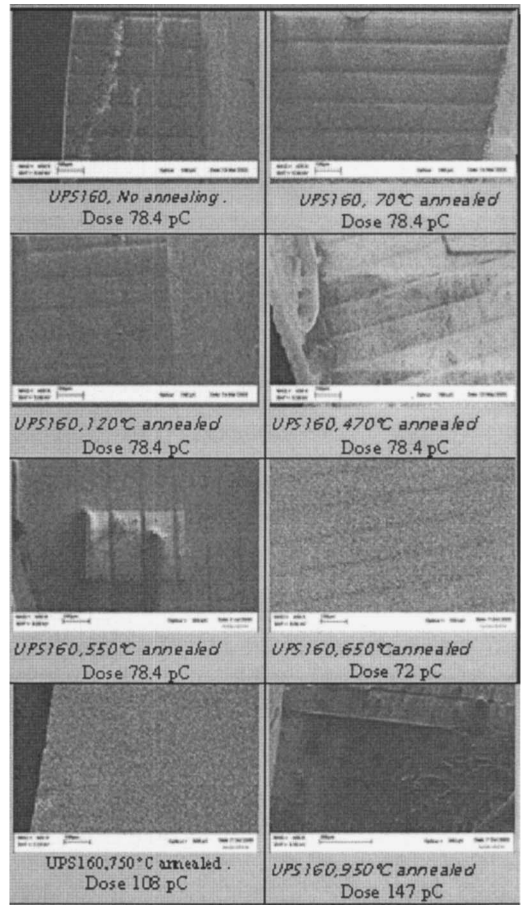

FIG. 1. Series of SEE photographs taken for a very small injected dose (78 pC, i.e., 1.65×10^4 pC/cm^2) when sample is isochronously annealed. The poled regions appear darker. There is a contrast at low temperature, which disappears progressively. Above 650 °C, no more contrast is detectable. The one seen above this temperature is due to the detachment of the film from the silicon substrate.

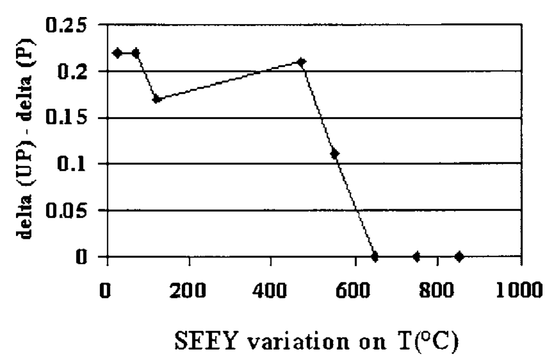

FIG. 2. Plot of the variation of the SEEY difference between poled and unpoled regions vs the annealing temperature. This difference between the two regions became zero at 650 °C.

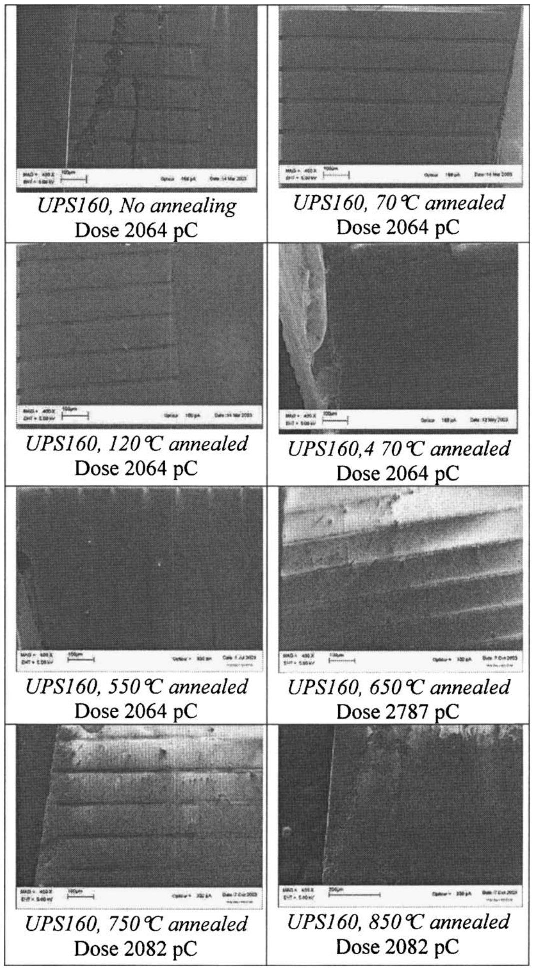

FIG. 3. Change on annealing temperature of SEE for a dose of 2000 pC, i.e., 4×10^5 pC/cm^2, i.e., when the SEE saturation (SEEY=1) is approached in all regions. We can see that the contrast begins to vanish above 550 °C. Then for larger annealing temperature, the reappearance of a contrast is due to deterioration of the layer.

us pointing out another property of the insulator: the trapping rate. The trapping rate appears to be larger in the unpoled region than in the poled one after annealing at 550 °C. This change can be accounted for by a change in the density of traps during the poling process. The displacement of ions or the introduction of more impurities during the poling process could be a possible explanation to the less density of available trapping sites in the poled material.

In conclusion, the secondary electron emission allows the investigation of the internal electric field produced by a stress, the trapping and transport of charges in insulators provided the SEE yield is measured with a good precision.[7] In

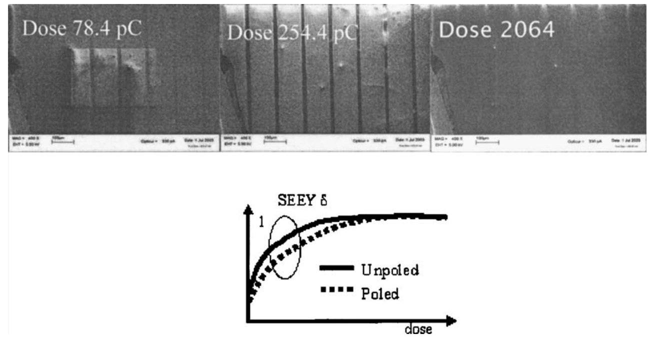

FIG. 4. Change on dose of the SEE for an annealing temperature of 550 °C. The contrast is small for a low dose especially at the beginning of the irradiation (78 pC, i.e., 1.65×10^4 pC/cm^2) because the poling electric field has vanished. A larger contrast is obtained for larger but intermediate dose (254 pC, i.e., 5×10^4 pC/cm^2). It is finally vanishing for very large doses (2000 pC, i.e., 4×10^5 pC/cm^2). The sketch of the δ curves deduced from the photographs shows that the contrast arises from a better trapping in the unpoled region than in poled one. For higher annealing temperature any contrast disappears.

the case of the study of the thermally poled Ge-doped silica films on silicon substrate it was deduced that the electric field induced by thermal poling is stable until 450 °C and is completely erased at 650 °C by measuring the SEEY at low dose. At large dose the change of the conductivity in high field due to the poling process was revealed, and at intermediate dose it was possible to identify important insulating properties related to the trapping rate. This one appears to be larger before poling than after.

This research work was financially supported by the GLAMOROUS project of the European Commission, contract IST-2000-28366.

[1]R. A. Myers, N. Mukherjer, and S. R. J. Brueck, Opt. Lett. **16**, 1732 (1991).
[2]M. R. Poulsen, P. I. Borel, J. Fage-Pedersen, J. Hübner, M. Kristensen, J. H. Povlsen, K. Rottwitt, M. Svalgaard, and W. E. Svendsen, Opt. Eng. **42**, 2821 (2003).
[3]H. Guillet de Chatellus, S. Montant, and E. Freysz, Opt. Lett. **25**, 1723 (2000).
[4]J. Jerphagnon and S. J. Kurtz, J. Appl. Phys. **414**, 1667 (1970).
[5]P. G. Kazansky, A. R. Smith, P. S. J. Russell, G. M. Yang, and G. M. Sessler, Appl. Phys. Lett. **68**, 269 (1996).
[6]F. Odiot, I. Marc, O. Granier, A. Michez, and A. Toureille, presented at the 3rd French Italian Symposium on SiO_2 and Advanced Dielectrics, Fuveau, France, June, 2000 (unpublished).
[7]D. Braga and G. Blaise, presented at the 4th International Conference on Electric Charges in Non-Conductive materials, Tours, France, 2001 (unpublished).
[8]Y. S. Liu, G. J. Zhang, W. B. Zhao, and Y. Zhang, Appl. Surf. Sci. **23**, 12 (2004).
[9]D. Braga, B. Poumellec, V. Cannas, G. Blaise, Y. Ren, and M. Kristensen, J. Appl. Phys. **96**, 885 (2004).